

EULER'S FORMULA AND PHASE RULE

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Abstract

The striking similarity of Euler's equation for simple polyhedra and Gibbs' phase rule has been discussed by several authors. Arguments have been advanced both for and against this analogy. We propose that the correspondence of the relations must be viewed as being due to the similarity of phase equilibrium systems to a special class of planar graphs and not to simple polyhedra. The proposed correspondence is demonstrated by parallel derivations of the two relations for the respective cases.

1. Introduction

The similarity between Euler's formula for simple polyhedra (1752) and Gibbs' phase rule (1870's) was noticed by Rudel [1] and Levin [2] and later discussed by Klochko [3], Mindel [4] and Rouvray [5]. Euler's formula relates the number of vertices (V), edges (E) and faces (F) in a simple polyhedron (one that can be continuously deformed into a sphere; for a description, see ref. [2]):

$$E - V + 2 = F. \quad (1)$$

Gibbs' phase rule, which has a similar statement,

$$C - P + 2 = f, \quad (2)$$

relates the number of components (C), phases (P) and degrees of freedom (f) of a chemical system at equilibrium.

Weinhold [6] has criticised this postulate of a similarity between simple polyhedra and chemical systems at equilibrium. He has shown that particular relationships suggested [4] to prove the correspondence between variables in eqs. (1) and (2) are unacceptable. It has also been pointed out [3,6] that since there are many chemical equilibrium systems for which there is no parallel among polyhedra, there can be no one-to-one correspondence between the two. Wildeboer and Plath [7] discuss surfaces of different genus, to represent a parallel to chemical equilibrium systems under external field influences and reaction conditions. We note that the reference [7] to graphs embedded on a sphere (planar graphs) is very relevant to the following discussion.

In this paper we show that a special class of planar graphs can be defined obeying eq. (1), raising the possibility of a correspondence with chemical equilibrium systems since they obey eq. (2). The correspondence is then demonstrated by parallel derivations of the two equations for the respective cases. These derivations reveal a homomorphism between (a) the new class of graphs and (b) chemical equilibrium systems, so that corresponding to every case of (b) there is at least one case of (a) and for every case of (a) there is one case of (b). Simple polyhedra are a special case of the new class of graphs, and therefore their correspondence to chemical equilibrium systems discussed in earlier literature is coincidental. Although the inductive sequences are different for building polyhedra and phase equilibrium systems [6], replacement of polyhedra by the new class of graphs achieves parallel sequences, as mentioned above. Also, the difficulty of not having polyhedra that correspond to some phase equilibrium systems [3,6] is overcome.

Some terms used in graph theory relevant to the present discussion are given below (more details can be found in any introductory textbook on graph theory, for example ref. [8]). A graph, simply stated, is a set of points (vertices) with a set of lines (edges) connecting pairs of them. If more than one edge connects a pair of vertices, they are called multiple edges. An edge connecting a vertex to itself is a loop. The degree of a vertex is the number of edges incident at it. If the edges are associated with a direction from one vertex to the other, then the graph is called a directed graph or a digraph. A graph is connected if each vertex can be reached from every other one through one or more edges and vertices. A cycle C^p is a connected undirected graph without any loops and multiple edges defined on V vertices, each of degree two. A planar graph is one that can be drawn on a plane without any of the edges intersecting; when the planar graph is drawn on the plane in such a way that the non-intersection of edges is clearly depicted, it is referred to as a plane graph.

In the following, we derive eq. (1) for planar graphs with multiple edges and/or loops, assuming a general definition of "face", by constructing the graphs from cycles by the addition or deletion of edges and the rearrangement of connectivities where necessary. All planar connected graphs with $F > 1$, connected graphs with $F = 1$ and disconnected graphs with two fragments ($F = 0$, as defined below) on V vertices can be obtained from cycles with the same number of vertices by adding edges, deleting one edge and deleting two edges, respectively, and making any rearrangement of connectivities that are needed. The family of graphs thus obtained will be referred to as "cycle-derived graphs". We also derive the phase rule for chemical systems at equilibrium using very similar procedures as those employed in the construction of cycle-derived graphs which obey the Euler relation. The similarity of the derivations for eqs. (1) and (2) will be taken as the basis for the proposed analogy between cycle-derived graphs and chemical systems at equilibrium. However, more than a numerical correspondence does not exist between variables of eqs. (1) and (2), as pointed out at the end of the paper. The possibility of adding multiple edges and/or loops in the cycle-derived graphs allows the number of edges to take arbitrarily large values. This is

necessary since, in principle, there is no limit on the number of components in a chemical system at equilibrium with a fixed number of phases.

Some connected planar graphs with $E \geq (3/2)V$, obtained by adding edges to cycles, are the collapsed (into two dimensions) forms of simple polyhedra. Therefore, as mentioned above, the original postulate of a similarity between simple polyhedra and systems at equilibrium is a special case of the more general approach presented here.

2. Derivation of eq. (1) for "cycle-derived graphs"

First of all, one has to formulate a general definition of "face" in a cycle-derived graph. Planarity of the graph is necessary for an unambiguous definition of the face. A segment of a plane, finite or infinite, bounded by a connected series of edges containing within it no part of the graph, will be counted as a face. Representing the planar graph as the corresponding plane graph facilitates the enumeration of the faces. Counting the infinite segment of a plane as a face is justified by the fact that the Euler-Schlaefli (1852) relationship (see, for example, ref. [6]), when applied in two dimensions, counts the areas inside and outside the polygon (singly connected polyhedron in two dimensions, i.e. a cycle) independently. We note that the "face" as defined here should be contrasted with the "region" in a planar graph [8]. The new definition provides for the possibility of zero face. We use the term face also because it helps to relate the present discussion to previous literature on the subject which deals with polyhedra.

Begin with a cycle C^V having V vertices and hence V edges. By definition, $F = 2$. If one edge is added between any two vertices (hence without changing the number of vertices), a new face is created which will be bounded by some of the edges already present and the new one added. Thus, for every edge added, a new face is also formed. This applies to loops and multiple edges as well. If $(E - V)$ edges are added, one obtains a graph with E edges. Since vertices have been untouched, this graph has V vertices. The total number of faces will be the first two plus $(E - V)$ new ones formed, i.e. $F = E - V + 2$ (fig. 1). To construct certain graphs, starting from a cycle

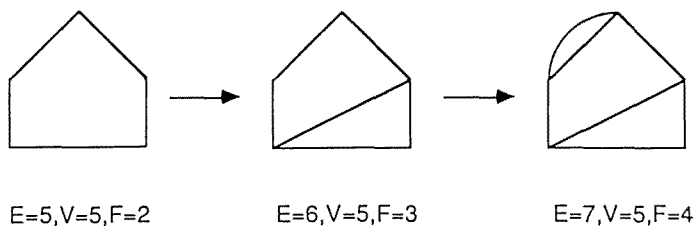


Fig. 1. Construction of a "cycle-derived graph" from the cycle C^5 .

C^V , some rearrangement of connectivities will have to be made. This involves opening out edges at some vertices and reconnecting them at others. In the first stage, one face

is lost, but it is regained at the second stage. If E and V are preserved, F is also preserved, and adherence to eq. (1) is maintained. One can thus construct any planar graph with $E \geq V$, starting from a cycle having V vertices; all such graphs will obey eq. (1).

To construct graphs with $E < V$ from a cycle, one simply has to remove edges (again retaining the number of vertices) one by one. When one edge is removed, one face is lost, and a chain graph is obtained. If one more edge is removed, two chain fragments or components (the component may sometimes be a single vertex only!) are obtained, and by definition $F = 0$. So, for every edge lost, a face is also lost, so that if one loses $(V - E)$ edges, $(V - E)$ faces are also lost. Thus, the final graph, which has V vertices and E edges, has $2 - (V - E)$, i.e. $E - V + 2$ faces. (See ref. [8] for an alternative proof.) Graphs with $(V - E) < 2$, i.e. $F < 0$, are not cycle-derived graphs and are not accommodated in the definition of the face given above. They are irrelevant to the current discussion.

Some connected planar graphs with $E \geq (3/2)V$ are the collapsed (into two dimensions) forms of simple polyhedra. If they are returned to three-dimensional form, polyhedra which still obey eq. (1) are obtained. In the process of going from two to three dimensions, the infinite face of the planar graph, bounded by the external edges,

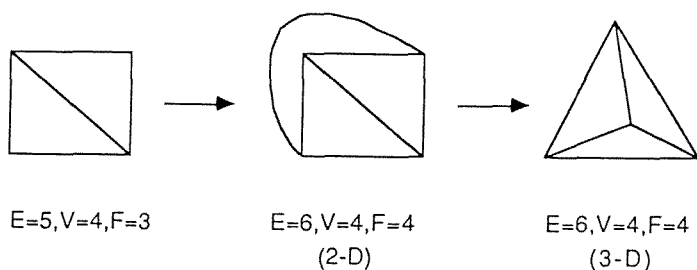


Fig. 2. Construction of the tetrahedron from the cycle C^4 .

is reconstructed as one of the faces of the polyhedron (see fig. 2 for the construction of a tetrahedron). This method may be used as another (see ref. [9]) simple proof of Euler's formula for simple polyhedra.

3. Analogous derivation of the phase rule

Consider a system at chemical equilibrium having C components in P phases. The phase rule states that it has $C - P + 2$ degrees of freedom (f). In other words, the system is defined by f independent variables. Such a system can be obtained, starting from a system composed of P components in P phases, as shown below.

The hypothetical system with P components in P phases with no mixing between them is equivalent to P independent chemical species. Only two variables are required to define any thermodynamic property of this system, say, temperature and pressure,

in order to specify Gibbs' free energy. Hence, $f = 2$. A real equilibrium system with P components in P phases can now be constructed by mixing each component into every phase. Now, no new degrees of freedom are obtained because when a component in, say, phase 1 is mixed into phase 2, its concentration in phase 2 (which could have been a new degree of freedom) is already fixed by its concentration in phase 1 due to equivalence of chemical potential. Once such an equilibrium system is obtained, one can construct the system with C components in P phases (with $C > P$) by adding new components without changing the number of phases. When one new component is distributed into the P phases, only one new degree of freedom is obtained, namely its concentration in any one of the phases. Its concentrations in the other phases are dependent on this first one. Thus, if $(C - P)$ new components are added, a system with C components and still P phases is obtained. However, now there will be $(C - P)$ new degrees of freedom in addition to the first two, so that $f = C - P + 2$. Thus, any system with $C \geq P$ can be constructed starting from the appropriate system with an equal number of components and phases, and all obey eq. (2) (for an example, see fig. 3).

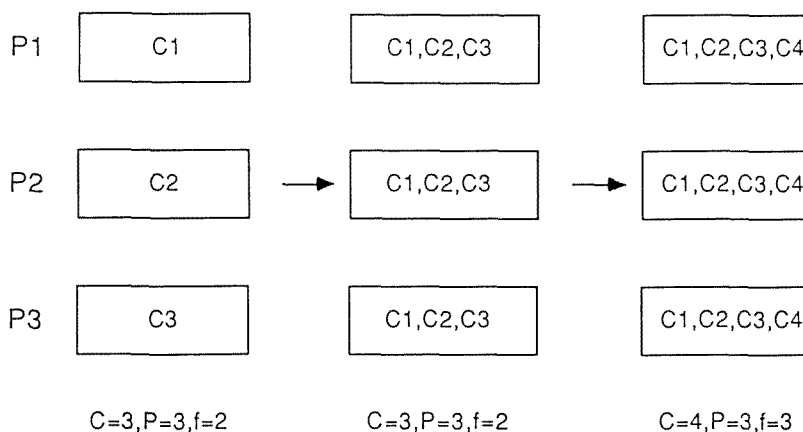


Fig. 3. Construction of a chemical system at equilibrium having three phases.

Assume a component is removed from the original system (with P components in P phases without mixing) without affecting the number of phases. This is possible only if one of the remaining components is distributed into the phase that has lost its component. This gives rise to a new equation of chemical potential, but no new concentration to be defined. This causes the loss of a degree of freedom. Further redistributions of components without changing C or P do not change f , as shown above. Removal of one more component decreases f by one again. Thus, if $(P - C)$ components are removed, retaining P phases, $(P - C)$ degrees of freedom are lost, causing f to become $2 - (P - C)$, i.e. $C - P + 2$.

It should be mentioned that this derivation of the phase rule is less elegant than the one originally given by Gibbs. Nevertheless, it runs parallel to that given above for the cycle-derived graphs, and hence suits the purpose of this discussion.

4. Correspondence between the two relations

We have shown that eqs. (1) and (2) can be obtained by very similar reasoning and processes. Cycle-derived graphs obeying eq. (1) are possible for all values of E and V such that $(V - E) \leq 2$, and chemical systems at equilibrium obeying the phase rule (eq. (2)) are possible for all values of C and P such that $(P - C) \leq 2$. Thus, we can establish the following correspondence between cycle-derived graphs and chemical systems at equilibrium: for every system at chemical equilibrium, there exists a cycle-derived graph, not necessarily a unique one, such that $C = E$, $P = V$ and $f = F$, and for every cycle-derived graph, there is a chemical equilibrium system, and both can be constructed by a very similar sequence of operations. Thus, there is a many-to-one mapping between the graphs and the chemical systems. However, there is no more than a numerical correspondence between, say, the edges and components or vertices and phases. The reason is the following. In the case of chemical systems, each component is present in every phase, however small the concentrations may be. In the graphs, on the other hand, each edge is associated with at most two vertices only, and each vertex need not be associated with every edge (in most cases, they are not). What this implies is that one cannot simply assign an exact correspondence of particular edges with components, vertices with phases, and faces with degrees of freedom. Correspondence is only between their numbers, and hence between the graph and the chemical system as a whole. This, we believe, limits the utility of a graphical representation of phase rule.

The difference in the inductive sequences leading to eqs. (1) and (2), pointed out by Weinhold [6], is evidently not present when one replaces polyhedra by cycle-derived graphs. The sequence described by eqs. (4.14) in [6] for chemical equilibrium systems can be applied in an identical form to cycle-derived graphs. When V is increased to $(V + 1)$, without a change in E , a disconnected graph is obtained and, hence, F goes to $(F - 1)$ in accordance with the definition of face in a cycle-derived graph. Further, one can see that the second problem mentioned in ref. [6], namely, the impossibility of polyhedra with E , V or F less than 4 does not arise here since, as shown above, cycle-derived graphs are well defined for such cases, even for F equal to zero! We believe, however, that the correspondence between topological and thermodynamic interpretation described by Mindel [4] cannot be valid, as pointed out in ref. [6].

The discussion in this paper is primarily meant to point out a way of overcoming the difficulties encountered in the treatments of the problem presented in previous literature. No utility of the analogy described has yet been established, and currently it is only of a pedagogical value. A possible extension of the work, keeping in view the feature noted in the previous paragraph, is to use hypergraphs to represent phase equilibrium systems. Attempts in this direction are in progress.

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